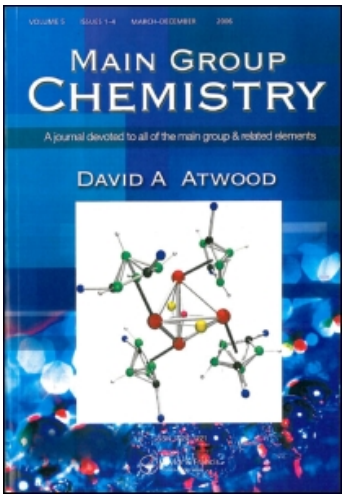

Main Group Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713722093

DFT and ^{1}H NMR molecular spectroscopic studies on biologically anti-oxidant active paramagnetic lanthanide(III)-chrysin complexes

Anees A. Ansari [a]
[a] National Physical Laboratory, Dr K. S. Krishnan Marge, New Delhi, India

Online Publication Date: 01 January 2008

To cite this Article Ansari, Anees A.(2008)'DFT and ^{1}H NMR molecular spectroscopic studies on biologically anti-oxidant active paramagnetic lanthanide(III)-chrysin complexes',Main Group Chemistry,7:1,43 — 56
To link to this Article: DOI: 10.1080/10241220801912637
URL: http://dx.doi.org/10.1080/10241220801912637

Main Group Chemistry
Vol. 7, No. 1, March 2008, 43 – 56

Taylor & Francis
Taylor & Francis Group

DFT and ^{1}H NMR molecular spectroscopic studies on biologically anti-oxidant active paramagnetic lanthanide(III)-chrysin complexes

ANEES A. ANSARI*

National Physical Laboratory, Dr K. S. Krishnan Marge, New Delhi, India

(Received 26 December 2007)

The interaction of trivalent lanthanide chlorides and chrysin in methanol results in formation of the complexes [Ln(chrysin)$_3$], where Ln = La, Pr, Nd, Sm, Gd, Tb and Ho. The complexes have been characterized by elemental analyses, molar conductance, IR, UV–Vis, TGA/DTA and NMR spectroscopic studies. They behave as non-electrolytes in DMF solution. The TGA data indicated that the complexes were anhydrous. The electronic spectra of the complexes were recorded in methanol DMF and DMSO solutions. ^{1}H NMR spectra of lanthanum, praseodymium, neodymium, samarium and gadolinium complexes have been studied in DMSO-d$_6$. ^{1}H NMR spectra of paramagnetic and diamagnetic complexes exhibit down-field as well as up-field shifts of chrysin resonances that shows a change in geometry during the ligand coordination to the metal ion. A theoretical study of the chrysin molecule was conducted through DFT, *ab initio*, and AM1 methods and this determined the coordination environment of the metal ions.

Keywords: Chrysin; Molecular mechanics; Density functional theory; ^{1}H NMR; UV–Vis

Introduction

In recent years great attention has been devoted to the design and synthesis of lanthanide coordination complexes with polyphenolic ligands such as flavonoids [1–14]. Flavonoids are polyphenolic organic compounds and are most frequently found in vegetable and other vascular plants that have potential applications in various fields of medical science [15–18]. Because of the presence of the hydroxyl and ketonic groups, they have strong chelating ability and bind to the metal ion in neutral solution. Several reports are available in the literature on flavonoids and their metal complexes with transition and non-transition metal ions [2–13]. It is known that polyphenolic ligands (flavonoids) play a very important role as anti-oxidants and demonstrate free radical scavenging ability [2–19]. The earlier studies examined the antioxidant activities of flavonoids and their metal complexes. They found that the suppression ratios of O_2 radicals for the metal complexes were mostly higher than with the ligand

*Corresponding author. E-mail: aneesaansari@gmail.com

Main Group Chemistry
ISSN 1024-1221 print/ISSN 1745-1167 online © 2008 Taylor & Francis
DOI: 10.1080/10241220801912637

alone [2–5,10–12]. This indicated that the inhibitory ratio of the free radicals in the polyphenolic complexes increased after complexation. Although free radicals may have useful physiological functions, they can damage biomolecules when generated in excess and are therefore implicated in the etiology of several diseases and ageing [18–22]. Another antioxidant mechanism of flavonoids may result from the interactions between transition metal ions and flavonoids to produce complexes that prevent the participation of these metal ions in free radical generating reactions [10–14].

In previous reports we have investigated quercetin and morin ligand lanthanide complexes to study their paramagnetic NMR shifts and their possible use as NMR shift reagents. The use of NMR spectroscopy to indicate the nature of bonding in paramagnetic complexes of metal ions is complicated by the difficulty in distinguishing between contact and pseudo-contact shifts. The contact shift can yield information relating to the extent of covalent bonding and to the mechanism of σ and π electron density delocalization in the paramagnetic species. The pseudo-contact shift can provide information relating to the geometrical configuration of ligands about a metal ion in solution and to metal-ion solvent molecule interactions. In continuation of our studies, we report here some complexes of trivalent lanthanides with chrysin (5,7-dihydroxyflavone).

N. Tang has reported the complex of chrysin with lanthanum acetate [5]. The complex was synthesized in aqueous ethanol solution and found to be an eight-coordinate complex where one acetate ion with two molecules of chrysin and two molecules of water were attached to the lanthanum metal ion in the inner coordination sphere. We found a different composition when the synthesis was carried out in non-aqueous solution with the lanthanides interacting with three chrysin molecules.

Experimental

Materials

Lanthanide oxides (99.9%, Lieco Chemicals, USA) were converted to the corresponding chlorides. Chrysin (99.9%, Sigma-Aldrich, USA), methanol, xylenol orange (SD Fine Chemicals), and EDTA (BDH) were used as such in this study.

Synthesis

Preparation of Ln (chrysin)$_3$ complexes. A hot solution of chrysin (3 m mol) in 50 mL methanol was mixed in magnetically stirred hot solution of hydrated lanthanide chloride (1 m mol) in 50 mL methanol and keeps the volume (100 mL) at 80°C temperature. After 1 hour stirring, yellow-colored needle-shaped crystal precipitate was formed. The precipitate was filtered and washed with methanol and dried under vacuum over P_4O_{10}.

Methods and physical measurements. Microanalysis (Carbon and Hydrogen) was carried out with a FI-SONS EA-1108 elemental analyzer. The metal content of the complexes were estimated by complexometric titration. The molar conductance of 10^{-3} M DMF solution of the complexes was measured by an Orion conductivity meter. The thermograms were recorded on a Du Pont TA 2000 TGA instrument under nitrogen at a heating rate of 10°C min^{-1}. Melting points (mp) were measured with a

Gallenkamp MBF-595 apparatus. A Shimadzu UV-2501PC spectrophotometer was used to obtain the electronic spectra in the region 200–700 nm in methanol, DMF and DMSO solvents. FTIR spectra in the 4000–400 cm^{-1} region was recorded from KBr pellets on a shimadzu-250 spectrophotometer. ^1H NMR chemical shift was measured in DMSO-d_6 solvent on Bruker 300 MHz spectrophotometer. Molecular modeling calculations were carried with an exchange-correlation STO-3G program in the Hyperchem (Version 7.5).

Results and discussion

The chrysin complexes of trivalent lanthanides have been isolated in methanol under normal conditions. The complexes are pale yellow polycrystalline solids. Some complexes have sharp melting points between the ranges 270–292°C, whereas some have no melting up to 360°C but decomposed after 290°C. The complexes are obtained as needle-shaped crystals and are soluble in common organic solvents, but are slightly soluble in water, ether, chloroform and CCl_4. The molar conductance of 10^{-3} M DMF solutions of the tris-complexes are low and suggest they are non-electrolytic in nature [23]. On the basis of elemental analysis (table 1), TGA/DTA, UV–Vis, IR and NMR spectral studies, we assumed that chrysin acted as a bidentate ligand and formed mononuclear complexes where one Ln(III) ion is bound to three chrysin molecules as shown in figure 1. These results suggest that the composition of the complexes is Ln(chrysin)$_3$.

UV–UV–Vis spectral analysis

The UV–Vis absorption spectra of chrysin and their metal complexes are measured in methanol, DMSO and DMF solution within the spectral range 200–700 cm^{-1}. The absorption spectra of free chrysin exhibits two major intense absorption bands in DMF, DMSO and methanol solutions in the ultraviolet region of the spectrum. The absorption in the 260–326 nm range correspond to the B ring portion (phenolic system band I) and is related to the π–π^* transitions within the aromatic ring of the ligand molecules. The measured energies and the extinction coefficients are comparable to this portion of the free ligand, which help us to assign that the band as a spin allowed (π–π^*) transition of the ligand. The second absorption transition observed between the spectral range 200–293 nm correspond to the A ring portion (quinolic system band II) which is due to π–π^*, n–π^* and n–σ^* transitions within the quinolic ring of the chrysin molecule [5,7–9]. These ligand-centered bands

Table 1. Physical properties of lanthanide-chrysin complexes.

Complex	Colour	MP (°C)	% Metal calculated (Observed)		
			C	H	M
La(chrysin)$_3$	Yellow	289–90	60.14 (61.28)	3.28 (3.50)	15.45 (16.0)
Pr(chrysin)$_3$	Yellow	>360 decomp.300°	60.01 (61.15)	3.02 (3.25)	15.64 (15.87)
Nd(chrysin)$_3$	Yellow	290–92	59.79 (58.78)	3.01 (3.41)	15.95 (16.50)
Sm(chrysin)$_3$	Yellow	279–80	59.39 (59.86)	2.99 (2.87)	16.52 (15.89)
Gd(chrysin)$_3$	Yellow	278–79	58.94 (60.46)	2.96 (3.05)	17.15 (16.69)
Tb(chrysin)$_3$	Yellow	>360 decomp 300°	58.83 (59.28)	2.96 (3.16)	17.30 (17.80)
Ho(chrysin)$_3$	Yellow	>360 decomp 300°	58.45 (59.28)	2.94 (3.12)	17.84 (18.12)

are accompanied by weaker transitions with lower energy extending into the visible region from 200 to 293 nm (figure 2). The absorption spectra of chrysin metal complexes are shifted towards higher wavelength in comparison to free chrysin ligand spectrum as shown in table 2. Such bathochromic shift can be explained by the extension of the conjugated system with the complexation. The UV–Vis absorption spectra of the complexes give significant information about the coordination sites of the chrysin molecule. As the 5-hydroxyl group has a more acidic proton and is deprotonated during complex formation, the 5-OH and 4-oxo groups are the sites which are involved in the complexation process. It confirms that the function of the proton of 5-OH group is in forming the complex. The absorption band II shifted more than band I, which indicates that band II (ring A, quinonolic system) is involved in coordination to the metal ion. The small shift of the bands in the spectrum of DMSO

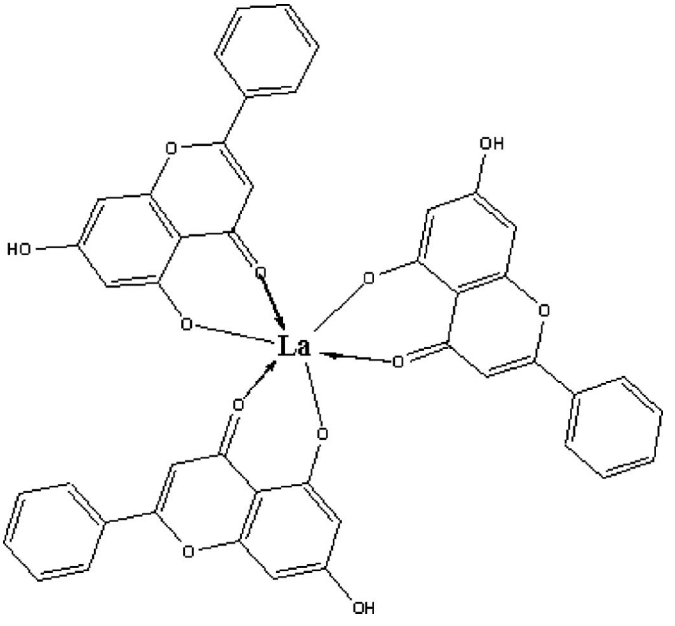

Figure 1. Proposed structure of $Ln(chrysin)_3$ complexes.

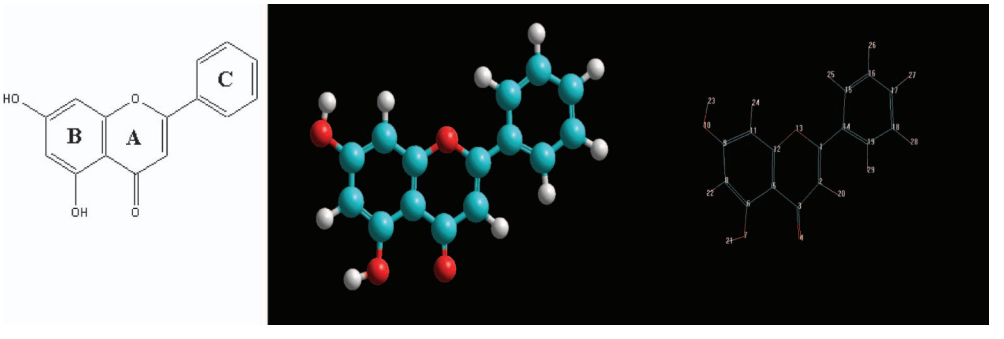

Figure 2. Structure of chrysin molecule and energy minimized.

Table 2. UV–Vis absorption spectral data of lanthanide-chrysin complexes.

Ligand/Complex	chrysin	La	Pr	Nd	Sm	Gd	Tb	Ho
Band I								
DMSO	–	316	315	316	320	326	322	326
DMF	315	315	314	314	315	317	merged	merged
MeOH	314	315	merged	315	315	316	merged	merged
Band II								
DMSO	269	272	273	271	293	275	271	272
DMF	–	277	272	277	278	279	272	277
MeOH	268	266	271	269	268	271	273	272
Band III								
DMSO	–	–	216	212	222	220	213	–
DMF	–	217	238	215	216	217	–	217
MeOH	218	219	219	218	226	214	216	226

and DMF solutions may be due to a de-metallation process taking place in the solution medium, because DMSO and DMF are highly coordinating solvent and have a very high Gutmann donor number [24–28].

IR Spectra

The IR absorption spectra of ligand and their lanthanide metal complexes have been recorded in the region 4000–400 cm^{-1}. The IR spectral data are summarized in table 3. Important information was obtained on comparing the ligand spectra with their complexes: e.g. ν(M–O) peaks appeared at 500–400 cm^{-1} while the ligand alone exhibited no such bands [30,31]. On the other hand, the bands in the region 3500–3000 cm^{-1} are attributed to the symmetrical and anti-symmetrical stretching modes of ν(O–H) in the spectrum of the ligand, which undergo change in the spectra of the complexes [29,30]. This is explained by the coordination of metal-oxygen bonding in this spectrum. The appearance of this frequency suggests the presence of hydroxyl group and shift of the ligand frequency, due to the loss of 5-OH group during the coordination to the lanthanide ion. The shift is also confirmed by the fact that the band loses its original characteristics after complexation in the complex spectrum (figure 3).

The ν(C–O–C) frequency and the ring skeletal vibrational stretching ν(C=C) frequency changed slightly upon complexation, indicating that the ring oxygen does not form metal-oxygen bonds with the lanthanide metal ion. However, a strong band at about 1653 cm^{-1}, detected in the spectra of the ligand is assigned to ν(C=O), which was highly affected (32–2 nm) and shifted in the spectrum of the metal complexes towards lower wave numbers. This further confirms the involvement of the ligand in the metal complexation. The significant displacement of ν(C=O) frequency and slight change in the ring breathing and ν(C–O–C) vibrations, shows that the coordination occurs through the C=O oxygen atom [5].

Thermal analysis

Thermogravimetric analyses of the complexes were carried out to examine the thermal stability, number and nature of water molecule(s) present. The thermograms

Table 3. IR absorption frequencies of lanthanide-chrysin complexes.

Functional Groups	Chrysin	La	Pr	Nd	Sm	Gd	Tb	Ho
ν(O–H)	3500–3000	3090	3370	3092	3095	3094	3360	3370
ν(C–H)	2926	2886	2928	2929	2887	2928	2930	2928
ν(C=O)	1653	1621	1647	1651	1653	1654	1652	1653
ν (C=C)	1611	1500	1492	1612	1612	1611	1611	1612
	1576			1576	1576	1577	1576	1576
	1553			1554	1554	1554	1553	1553
δ(O–H) C–O–H	1450	1453	1449	1448	1449	1449	1449	1449
ν(C–O)	1356	1356	1357	1357	1356	1357	1355	1356
C–O–C	1313		1313	1312	1313	1313	1312	1313
C–C–O								
ν (C–C)	1245;	1164	1169	1168	1168	1168;	1168;	1168;
C–C–C	1168					1120	1100	1101
‖								
O								
ρ (O–H) in plane deformation	1029	1026	1032	1030	1031	1032	1030	1030
(C–H) in plane deformation	907	905	908	907	907	907	907	907
(C–C) in plane deformation	841	840	842	840	841	841	839	841
(O–H) out of plane deformation	806	803	807	806	806	806	806	806
(C–H) out of plane deformation	782	778	782	782	782	782	782	782
	731	734	732	731	731	732	731	731
(C–C) out of plane deformation	692	639	642	641	641	692	692	692
	641	504	612	611	612	641	641	641
	509			502	510	510	510	510
M–O	–	429	430	429	430	429	429	430

were recorded for all the complexes in the temperature range 30–600°C in nitrogen atmosphere and their data are collected in the table 4. The thermogram of all the complexes shows similar behaviour in the TGA spectrum. Thermal spectra of the complexes revealed that the complexes are stable up to 300°C and do not show any weight loss below this temperature. It is strong evidence, which represent that the complexes are devoid of lattice water as well as coordinated water in the coordination sphere. The TGA curve shows that the first weight loss of the complexes was observed between the range 28.15–27.38%, which occurs between the temperature 327–289°C, corresponding to one molecule of chrysin. After the elimination of the first molecule, the decomposition of the second and third molecules of chrysin started simultaneously between the temperature 534–505°C. The observed weight loss 55.49–50.95%, is equivalent to two molecules of chrysin (calculated wt. loss for two molecule of chrysin is 56.31–54.77). A DTA curve was observed at this temperature (figure 4).

^{1}H NMR spectral

^{1}H NMR spectral studies have been carried out to investigate the solution structure of the lanthanide chrysin complexes and their stability in the solution medium. The ^{1}H NMR spectra of ligand and their lanthanide metal complexes (lanthanum, praseodymium, neodymium, samarium and gadolinium) were measured in DMSO-d_6 solution. ^{1}H NMR resonance signals with their tentative assignments are based on the

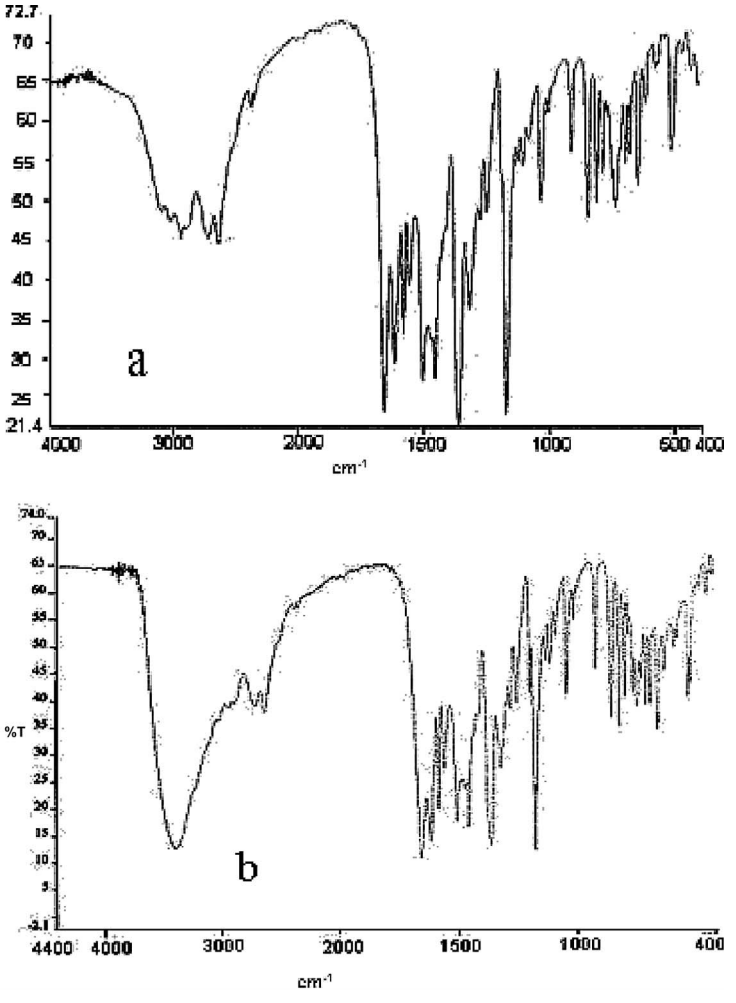

Figure 3. FTIR spectra (a) chrysin ligand and (b) La(chrysin)$_3$.

reports available in the literature [5] and their data are summarized in table 5 and paramagnetic shift data also given in table 6. The proton NMR spectra of the lanthanum, praseodymium and neodymium are shown in figures 5, 6, and 7, respectively. The resonance signals of coordinated chrysin are found to shift downfield as well as up field as compared with the free chrysin molecule. The shifts are comparable to other diamagnetic lanthanum complexes of flavonoids in DMSO-d_6 [6,32]. Figure 5 shows the relative shift in the ^{1}H NMR signals for the La(III) with respect to the free ligand precursor. Lack of free ligand precursor peaks and observed shifts in the spectrum conclusively indicates the binding of the ligand to the metal ions. The 5-OH proton resonance signal was not observed in the spectrum of all complexes (figure 5). Disappearance of this resonance signal in the complex spectrum indicates that 5-OH proton loses during the complexation process and this phenolic group participates in coordination to the metal ion. The proton resonance signals which are

Table 4. Thermal analysis data of lanthanide-chrysin complexes.

Complexes	Temperature (°C)	% Weight loss		Constituents eliminated
		Calc.	Obs.	
La	314	28.15	27.23	1 molecule of chrysin
	526	56.31	51.86	2 molecules of chrysin
Pr	290	28.11	31.86	1 molecule of chrysin
	526	56.23	50.95	2 molecules of chrysin
Nd	327	28.01	30.96	1 molecule of chrysin
	526	56.02	52.18	2 molecules of chrysin
Sm	289	27.82	26.41	1 molecule of chrysin
	520	55.65	54.28	2 molecules of chrysin
Tb	315	27.56	29.58	1 molecule of chrysin
	505	55.13	52.34	2 molecules of chrysin
Ho	289	27.38	25.78	1 molecule of chrysin
	534	54.77	55.49	2 molecules of chrysin

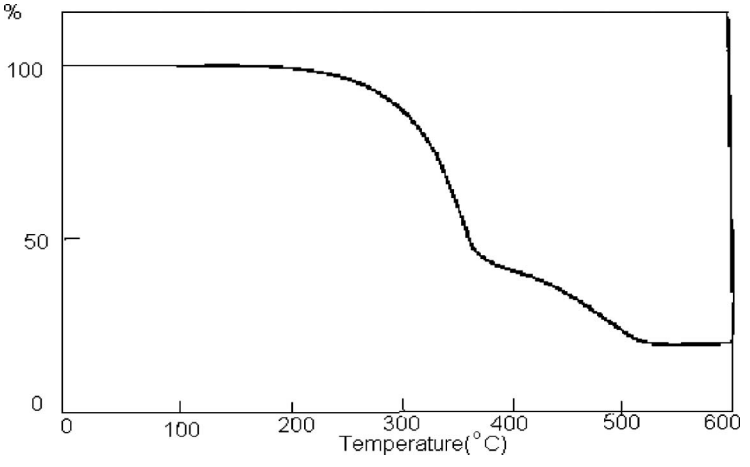

Figure 4. TGA spectra of La(chrysin)$_3$ complex.

Table 5. ^{1}H NMR chemical shift data of lanthanide-chrysin complexes in DMSO-d$_6$ on 300 MHz.

Compounds/Ligand	Chemical Shifts (Paramagnetic shifts)							
	7-OH	5-OH	H-2′&6′	H-3,4′&5′	H-4′	H-3	H-8	H-6
Chrysin	12.83s[a]	10.91s	8.08	7.62m	7.55	6.97s	6.52s	6.22s
La	12.82	–	8.05d	7.64m	7.56s	6.96s	6.53s	6.23s
Pr	12.44	–	7.70s	7.34d	7.51s	6.43	6.27	6.06
Nd	12.75	–	8.05s	7.60s	merged	6.89d	6.53	6.24
Sm	12.65	–	7.88d	7.52d	7.45s	6.61	6.46	6.30
Gd	12.55	–	7.78d	7.43d	7.28s	6.52	6.37	6.23

Chemical shift and paramagnetic shifts are expressed in ppm (δ); s: singlet; d: doublet; m: multiplet.
The negative sign indicates an up field shift and positive shifts are downfield to TMS.
[a and b]references [17] and [19].

shifted to down fields are subjected to no perturbing influence other than the deshielding expected from the electron withdrawing inductive effect of coordination. Small chemical shift was measured in the spectrum of La (III) complex. Generally diamagnetic metal ions revealed small chemical shift. The small chemical shifts of chrysin proton resonance signals may be due to they are weakly coordinated to the metal ion in this solvent (DMSO) (figure 5). These proton NMR spectrum results suggest that DMSO is a strongly coordinating solvent, which coordinates to the metal ion and replace the ligand from the coordination sphere and form the complex [24–28]. Because Ln(III) ions have a lower affinity for chrysin, the Ln-O covalent coordinate bond might be replaced by DMSO-Ln. The UV–Vis spectra results also suggest that DMSO is strongly coordinating solvent [24–28].

On the other hand, the spectrum of paramagnetic complexes are very interesting where free chrysin proton resonances have been shifted up-field (except H-6, in the case of Nd) as compared with the diamagnetic analogue (figure 7). Substantial changes are produced in the chemical shift of chrysin proton resonance signals in the paramagnetic complex spectrums. In the spectrum of paramagnetic complexes the chrysin signals

Table 6. Paramagnetic shifts on lanthanide-chrysin complexes in DMSO-d_6.

Compounds	7-OH	H-2′&6′	H-3′,4′&5′	H-4′	H-3	H-8	H-6
Pr	−0.38	−0.35	−0.30	−0.04	−0.53	−0.26	−0.17
Nd	−0.07	0.00	−0.04	–	−0.07	0.00	0.01
Sm	−0.17	−0.17	−0.12	−0.11	−0.35	−0.07	0.07
Gd	−0.27	−0.27	−0.21	−0.28	−0.44	−0.16	0.00

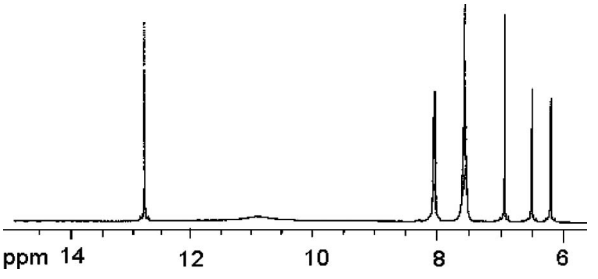

Figure 5. ^{1}H NMR spectra of La(chrysin)$_3$ complex.

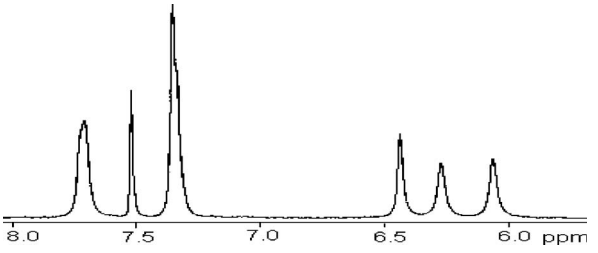

Figure 6. ^{1}H NMR spectra of Pr(chrysin)$_3$ complex.

were broad and induced high field shift compared with their diamagnetic analogues. These protons have been shifted to high fields but lie within the TMS envelop. The shifts decrease with increasing distance of the protons from the metal ion and is largest for the H-3 protons ($\delta = -0.53$) and least for H-4′ ($\sigma = -0.04$). No evidence of the free ligand in the complexes spectrum is observed as shown in the figures 7 and 8. Remarkably, different spectral features are found in the case of the H-3′, 5′ and 4′ proton resonance signals in the paramagnetic complex spectrum (figures 7 and 8). That the proton H-3′, 5′ and 4′ are strongly coupled and broad resonance to give a single peak in Nd spectrum (figure 7) while this signal was split in praseodymium, samarium and gadolinium spectrum and revealed a very high field shift. This increases with an increase in unpaired electrons in the 4f-orbitals. The large broadening in the case of Nd is, of course, due to the long electron relaxation time of Nd (figure 7) compared with praseodymium [33] (figure 6). The differences in the relative line broadening reflect different metal-proton distances, the broader peaks being associated with the proton nuclei of ligand closer to the lanthanide ions and these broad resonances supports the predicted octahedral geometry of the complexes. This kind of octahedral geometry has discussed by Bianconi group [32]. These observations indicate that aromatic ring coordinate to the metal ion through phenolic and carbonyl groups.

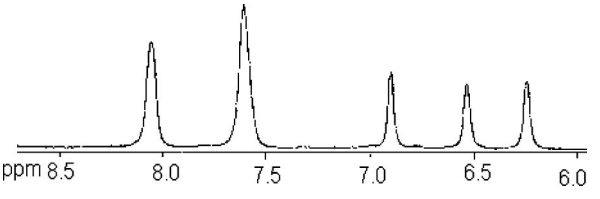

Figure 7. ^{1}H NMR spectra of Nd(chrysin)$_3$ complex.

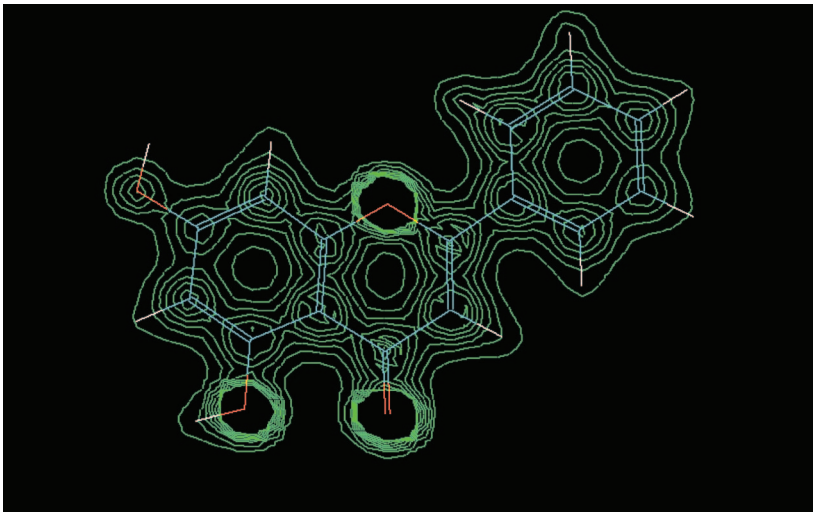

Figure 8. Charge density contour diagram of chrysin obtained by using semiempirical (PM3) and *ab initio* methods.

Paramagnetic shifts in the case of lanthanides are predominantly from dipolar mechanism. This may be verified if the ratio Rij of the shift of the nucleus i to another j in the same molecule remains the same for all the lanthanides [32,33]. The ratio of the chemical shifts of the protons H-8 and H-6 are 1.03, 1.04, 1.02 and 1.02; of the H-2′ and 6′ and H-3′, 5′ and 4′ are 1.05, 1.05, 1.04 and 1.04 for the complexes of praseodymium, neodymium, samarium and gadolinium complexes, respectively. The ratios are similar, for a given set of protons and therefore, the shifts owe their origin to dipolar interaction [34,35]. We note that ratios of the chemical shifts induced by different metal ions in the complexes are similar for chrysin protons. The ratios for Pr/Nd are 0.97, 0.95, 0.96, 0.93, 0.96 and 0.97 for the 7-OH, H-2′&6′, H-3′5′&4′, H-3, H-8 and H-6, respectively. Thus we conclude that the paramagnetic shift, though small in magnitude in these complexes are exclusively due to dipolar interaction [33–35].

Computational details

Computational chemistry is an established laboratory tool to investigate the optimized geometrical structure of the organic and inorganic compounds in the gaseous phase. We used several programs DFT, *a*b initio, AM1 and MM^{+} for theoretical calculations of chrysin ligand and their complexes [36]. Density functional calculations of chrysin molecule exhibit the presence of greater electron charge density on the (C=O) group oxygen atom and 5-OH group oxygen atoms than the 1-(C–O–C) and 7-OH group oxygen atoms. They also indicate that carbonyl group has a stronger $\pi-$donor character than (C–O–C). These DFT calculations of chrysin molecule are agreed with the spectroscopic (UV–Vis, IR and ^{1}H NMR) results (figures 8 and 9).

Theoretical modeling of the Ln(chrysin)$_3$ complexes in the gas phase using density functional theory provides optimized octahedral geometrical structure that almost perfectly fit the spectroscopic structures. Molecular modeling of the octahedral complex (table 7) suggests close contact interactions for H-3 proton and H-2′ and 6′ protons of the chrysin ligand as the phenyl substituents attempts to rotate. The observation of NMR spectroscopy broadening is only these two sets of protons are strongly supportive of the predicted structure.

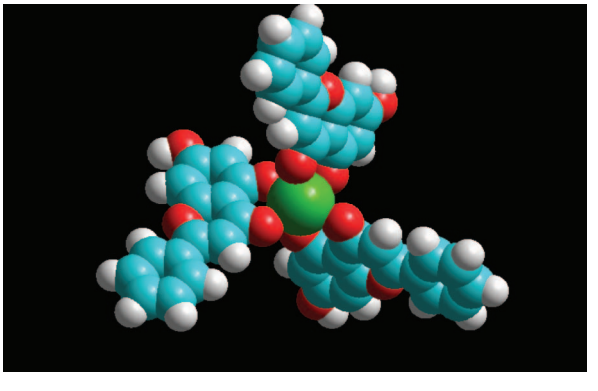

Figure 9. Energy minimized structure of Ln(chrysin)$_3$ complexes.

Table 7. Optimized geometrical parameters of chrysin obtained by density functional theory with STO-3G functional set.

Bond length	Value (Å)	Bond angle	Value (Å)
C(1)–C(2)	1.3562	C(2)–C(3)–O(4)	126.041
C(2)–H(20)	1.08	C(5)–C(3)–O(4)	126.073
C(2)–C(3)	1.4382	C(5)–C(6)–O(7)	123.761
C(3)–O(4)	1.2138	H(21)–O(7)–C(6)	109.471
C(3)–C(5)	1.4934	C(8)–C(6)–O(7)	122.798
C(5)–C(12)	1.4165	C(8)–C(9)–O(10)	127.599
C(12)–O(13)	1.3866	C(9)–O(10)–H(23)	109.471
O(13)–C(1)	1.3933	C(11)–C(9)–O(10)	127.5
C(5)–C(6)	1.4893		
C(6)–C(8)	1.4315		
C(6)–O(7)	1.2285		
O(7)–H(21)	0.96		
C(8)–H(22)	1.08		
C(8)–H(9)	1.4325		
C(9)–O(10)	1.2256		
O(10)–H(23)	0.96		
C(9)–C(11)	1.4470		
C(11)–H(24)	1.08		
C(11)–C(12)	1.3909		
C(1)–C(14)	1.4318		
C(14)–C(15)	1.4226		
C(15)–H(25)	1.08		
C(15)–C(16)	1.3476		
C(16)–H(26)	1.08		
C(16)–C(17)	1.3225		
C(17)–H(27)	1.08		
C(17)–C(18)	1.4145		
C(18)–H(28)	1.08		
C(18)–H(19)	1.3933		
C(19)–H(29)	1.08		
C(19)–C(14)	1.3895		

Conclusion

We have successfully carried out the synthesis, spectroscopic studies and structural determination of lanthanide-chrysin complexes. These complexes are isostructural with similar coordination geometries around the metal center. The results of spectral studies (^{1}H NMR, IR, TGA and UV–Vis) and molecular modeling provide evidences coordination of ligand and indicate that 4-oxo and 5-OH groups are hosting sites of chrysin ligand for binding to the metal ion. The absence of a water molecule in the coordination sphere was confirmed by the study of thermogravimetrically.

A detailed ^{1}H NMR study has allowed a complete assignment of the proton resonance for both diamagnetic and paramagnetic species. The overall patterns of the NMR spectra are consistent with the maintenance in solution of the coordination features. The spectroscopic data demonstrated the coordination behaviour of these complexes which are heavily influenced by the binding of chrysin molecule.

Acknowledgement

Author (AAA) thanks CSIR for financial support, which is gratefully acknowledged.

References

[1] D.R. Williams. Metals, ligands, and cancer. *Chem. Rev.*, **72**, 203 (1972).
[2] J.P. Cornard, J.C. Merlin. Spectroscopic and structural study of complexes of quercetin with Al(III). *J. Inorg. Biochem.* **92**, 19 (2002).
[3] J. Kang, L. Zhou, X. Lu, H. Liu, M. Zhang, H. Wu. Electrochemical investigation on interaction between DNA with quercetin and Eu–Qu3 complex. *J. Inorg. Biochem.* **98**, 79 (2004).
[4] J. Zhou, L.F. Wang, J.-Y. Wang, N. Tang. Synthesis, characterization, antioxidative and antitumor activities of solid quercetin rare earth(III) complexes. *J. Inorg. Biochem.* **83**, 41 (2001).
[5] Y.B. Zeng, N. Yang, W.-S. Liu, N. Tang. Synthesis, characterization and DNA-binding properties of La(III) complex of chrysin. *J. Inorg. Biochem.* **97**, 258 (2003).
[6] A.A. Ansari, K. Iftikhar. Optical absorption and NMR spectroscopic studies on paramagnetic neodymium(III) complexes with β-diketone and heterocyclic amines The environment effect on 4f–4f hypersensitive transitions. *Spectrochimica Acta Part A*, **67**, 1178 (2007).
[7] M.E. Bodini, M.A. delValle, R. Tapia, F. Leighton, P. Berrios. Zinc catechin complexes in aprotic medium. Redox chemistry and interaction with superoxide radical anion. *Polyhedron*, **20**, 1005 (2001) and reference there in.
[8] E.B. Hergovich, J. Kaizer, G. Speier, G. Huttner, A. Jacobi. Preparation and oxygenation of (flavonolato)copper isoindoline complexes with relevance to quercetin dioxygenase. *Inorg. Chem.* **39**, 4224 (2000).
[9] L.J. Porter, and K.R. Markham. The aluminum (III) complexes of hydroxyflavones in absolute methanol. Part II. Ligands containing more than one chelating site. *J. Chem. Soc. C*, 1309 (1970).
[10] Z. Qi, W. Liufang, L. Xiang. Synthesis, characterization and antitumour properties of metal(II) solid complexes with morin. *Trans. Metal Chem.*, **21**, 23 (1996).
[11] Y. Song, P. Yang, M. Yang, J. Kang, S. Qin, B. Lu. Spectroscopic and voltammetric studies of the cobalt (II) complex of morin bound to calf thymus DNA. *Trans. Metal Chem.*, **28**, 712 (2003).
[12] A. Bravo, J.R. Anacona. Metal complexes of the flavonoid quercetin: antibacterial properties. *Trans. Metal Chem.*, **26**, 20 (2001).
[13] J. Zhou, L. Wang, J. Wang, N. Tang. Antioxidative and anti-tumour activities of solid quercetin metal(II) complexes. *Trans. Metal Chem.*, **26**, 57 (2001).
[14] R.F.V. de Souza, W.F. De Giovani. Synthesis, spectral and electrochemical properties of Al(III) and Zn(II) complexes with flavonoids. *Spectrochimica Acta Part A* **61**, 1985 (2005).
[15] M. Foti, M. Piattelli, M. Tiziana, G. Ruberto. Flavonoids, coumarins, and cinnamic acids as antioxidants in a micellar system structure-activity relationship. *J. Agric. Food Chem.* **44**, 497 (1996).
[16] S.A.B.E. van Acker, G.P. van Balen, D.J. van den Berg, A. Bast, W.J.F. van der Vijgh. Influence of iron chelation on the antioxidant activity of flavonoids. *Biochem. Pharmacol.* **56**, 935 (1998).
[17] S.R. Husain, J. Cillard, P. Cillard. Hydroxyl radical scavenging activity of flavonoids. *Phytochemistry*, **26**, 2489 (1987).
[18] P.C.H. Hollman, M.B. Katen. Dietary flavonoids: intake, health effects and bioavailability. *Food Chem. Toxicol.* **37**, 937 (1999).
[19] C.L.M. Chantal, V.M. France, T. Moriel, S.M. Halene, M. Jacques, S.W. Marc. Comparative effects of flavonoids and model inducers on drug-metabolizing enzymes in rat liver. *Toxicology*, **114**, 19 (1996).
[20] K. Ishinge, D. Schubert, Y. Sagara, Flavonoids protect neuronal cells from oxidative stress by three distinct mechanisms. *Free Radi. Biol. Med.*, **30**, 433 (2002).
[21] A. Saija, M. Scalese, M. Lanza, D. Marzullo, F. Bonina, F. Castelli. Flavonoids as antioxidant agents: importance of their interaction with biomembranes. *Free Radi. Biol. Med.*, **19**, 481 (1995).
[22] M.M. Silva, M.R. Santose, G. Caroco, R. Rocha, G. Justino, L. Mira. Structure-antioxidant activity relationships of flavonoids: a re-examination. *Free Radical Res.*, **36**, 1219 (2002).
[23] W.J. Geary. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coord. Chem. Rev.*, **7**, 81 (1971).
[24] V. Gutmann. Solvent effects on the reactivities of organometallic compounds. *Coord. Chem. Rev.*, **18**, 225 (1976).
[25] V. Monga, B.O. Patrick, C. Orving. Group 13 and lanthanide complexes with mixed anionic ligands derived from maltol. *Inorg. Chem.*, **44**, 2666 (2005).
[26] U. Casellato, S. Tamburini, P. Tomasin, P.A. Vigato, S. Aime, M. Botta. Synthesis, x-ray structure, and solution NMR studies of Ln(III) complexes with a macrocyclic asymmetric compartmental schiff base preference of the Ln(III) ions for a crown-like coordination site. *Inorg. Chem.* **38**, 2906 (1999).
[27] X.P. Yang, B.-S. Kang, W.K. Wong, C.Y. Su, H.Q Liu. Syntheses, crystal structures, and luminescent properties of lanthanide complexes with tripodal ligands bearing benzimidazole and pyridine groups. *Inorg. Chem*, **42**, 169 (2003).

[28] H.A. Hussain, A.A. Ansari, K. Iftikhar. Optical absorption and NMR spectroscopic studies on paramagnetic trivalent lanthanide complexes with 2,2_-bipyridine. The solvent effect on 4f–4f hypersensitive transitions. *Spectrochim. Acta part A*, **60**, 873 (2004).
[29] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd edition, 264p, Wiley, New York (1978).
[30] J.R. Ferraro, W.R. Walker. Infrared spectra of hydroxy-bridged copper(II) compounds. *Inorg. Chem.*, **4**, 1382 (1965).
[31] V.T. Kasumov, E. Taş, F. Köksal, Ş.Ö. Yaman. Synthesis, characterization, redox behavior and hydrogenation catalytic activity of bis(N-aryl–3,5-Bu_2'-salicylaldiiminenato)palladium(II) complexes. *Polyhedron*, **24**, 319 (2005).
[32] D.P. Long, A. Chandrasekheran, R.O. Day, P.A. Bianconi, A.L. Rheingold. Yttrium and neodymium di- and monohalide complexes based on scorpionate (Poly(pyrazolyl)borate) ligands. *Inorg. Chem.*, **39**, 4476 (2000).
[33] C.D. Berry, J.A. Glasel, A.C.T. North, R.J.P. Wiliams, A.V. Xavier. Quantitatite determination of mononucleotide conformations in solution using lanthanide ion shift and broadening NMR probes. *Nature*, **232**, 236 (1971).
[34] G.N. La Mar, W.D. Horrocks Jr., R.H. Holm, editors. *NMR of Paramagnetic molecules, Principles and Applications*, Academic press, New York (1973).
[35] B. Bleaney. Nuclear magnetic resonance shifts in solution due to lanthanide ions. *J. Mag. Resonance*, **8**, 91 (1972).
[36] Hypercube, Inc., USA.